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(71) Applicant: PIGMENTI ITALIA S.p.A., Via Marconato, 8, I-20031 Cesano Maderno (Milano) (IT)

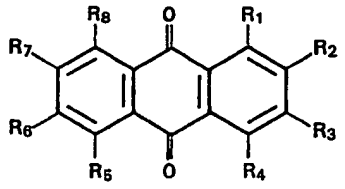
(72) Inventor: Prandi, Carlo, 6 Via Donegani, I-20020 Cogliate Milan (IT)
Inventor: Osti, Alberto, 53 Via Rombon, I-20134 Milan (IT)

(74) Representative: Hirsch, Marc-Roger, Cabinet Hirsch 34 rue de Bassano, F-75008 Paris (FR)

(54) **Marking and denaturing composition, particularly suitable for marking and denaturing diesel oil and similar oil products.**

(57) The invention relates to a marking and denaturing composition, particularly suitable for marking and denaturing diesel oil and similar oil products.

The said composition contains an anthraquinone derivative having the formula:



where R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 identical or different, represent a hydrogen atom, a halogen atom or an alkyl, cycloalkyl or arylalkyl radical having from 1 to 12 carbon atoms.

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MARKING AND DENATURING COMPOSITION, PARTICULARLY SUITABLE FOR MARKING AND DENATURING DIESEL OIL AND SIMILAR OIL PRODUCTS

BACKGROUND OF THE INVENTION

The invention relates to a marking and denaturing composition, particularly suitable for marking and denaturing diesel oil and similar oil products.

There is currently a need for marking oil products (for example fuels or industrial solvents) due to the difference in price at which that same product may be offered for sale. Indeed, as a consequence of different rates of taxation, diesel oils intended e.g. for agricultural purposes, or diesel oils intended for the fishing industry are taxed at a lower rate than diesel oil intended for road vehicles and such a situation is liable to give rise to fiscal fraud, when the product is furnished for purposes different to those provided for by the fiscal regulations. This is in fact why the products are usually marked by means of suitable compounds, which allow an easy identification. An ideal marker or marking composition should exhibit the following features:

- a satisfactory stability under conditions of normal use;
- no impairing of the physico-chemical features of the petroleum fuel or of the solvent;
- a solubility sufficient to allow use in the form of a concentrated solution;
- very low chances of being eliminated by means of physical or chemical methods;
- possibility of being used in small quantities;
- possibility of being identified by means of simple, quick and very sensitive methods;
- absence of negative toxicological features.

Not all proposed or used marking compositions can completely

satisfy such requirements. In fact, the best known markers are:

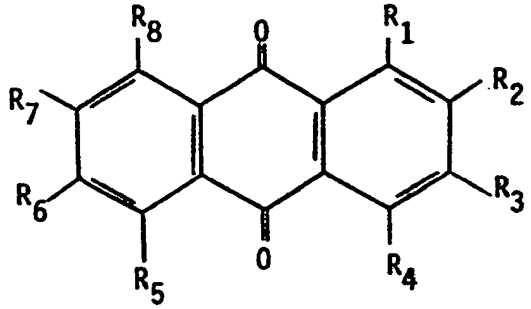
- radioactive substances, requiring particular care, during handling, because of physiological dangers;
- metallorganic compounds, generally showing a poor stability during storage;
- furfural, which could also be present as traces naturally occurring in the oil cuts, and thus give rise to a positive test due simply to the particular kind of analysis (furfural, moreover, shows poor stability);
- diphenylamine, which can be rather easily eliminated; since it is an amino-aryl compound, diphenylamine must be handled in a carefully strictly controlled zone;
- primary, secondary or tertiary arylamines, which can easily be extracted by means of diluted acids; as with the case of diphenylamine, their handling is controlled by very strict regulations;
- naphthols, which could already be present within the oil cuts and which can easily be eliminated.

U.S. patent 4 209 302 discloses the use of naphtylamine derivatives. However, these compounds do not completely satisfy the requirements herein-above, especially because they can easily be extracted from the marked product.

The applicant has now found a new marking composition allowing an unexpected and unforeseen reduction of the drawbacks herein-above.

DISCLOSURE OF THE INVENTION

In its widest form the invention concerns a marking and denaturing composition, particularly suitable for diesel oil and for similar oil products, containing an anthraquinone derivative having the formula:



where R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 identical or different, represent a hydrogen atom, a halogen atom or an alkyl, cycloalkyl or arylalkyl radical having from 1 to 12 carbon atoms.

Oils products similar to diesel oil are, for example, gasoline, kerosene oil and lamp oil.

The amounts of anthraquinone derivative to be used as a marker can vary within wide limits and the minimum value merely depends upon the identification test. By using the simple and rapid test described herein-after, concentrations as low as 1 to 3 ppm can be used.

Generally, a greater amount is added, in order to obtain in any case a positive result and also to foresee the case where the marked product is diluted at the time the fraud occurs. From a practical point of view, from 1 to 300 ppm (and preferably 3-50 ppm) can be used.

The advantages inherent within the present anthraquinone derivative having formula (I) are the following:

- no counter-indications of toxicological nature;
- considerable stability with respect to the oil product to be marked;
- difficulty to eliminate the said marker from its solutions within the oil products, by means, for example, of adsorption techniques on active carbons, alumina, decoloring earth or silica gel;
- no modification of color of the oil product, whereby the presence within diesel oil can be ascertained only when carrying out a specific test;
- it can be identified and determined quantitatively by means of very simple methods that do not require complicated devices and can be carried out by unskilled personnel;
- it can be handled either as a solid or as a solution in organic solvents, optionally in admixture with other colored or colorless markers.

The markers according to the present invention should be prescribed, in particular, when an anthraquinone dye and/or an azoic dye is present; best results are obtained when using said markers or marking compositions in admixture with furfural and/or with other suitable organic solvents, for example xylenes, these xylenes generally acting as a diluent.

As to the mothod of identifying the products it is preferable to operate according to the following method:

- 10 cm^3 of acetone and 5 cm^3 of an aqueous and alkaline solution of sodium dithionite are added to 200 cm^3 of marked diesel oil which is thereafter stirred and left to decant for 5-10 minutes, whereby the bottom layer presents a red color characteristic of the

anthraquinone derivative according to formula (I).

The following examples illustrate the invention, without however in any way limiting its scope.

EXAMPLE 1

1 g of 2-ethyl-anthraquinone was added to 100 cm^3 of a mixture of xylenes and to 3 cm^3 of the solution thus obtained a diesel oil, intended for motorboats, was added until 1 liter volume was obtained, i.e. a solution containing 30 mg/dm^3 (30 ppm) of 2-ethyl-anthraquinone. Thereafter, 10 cm^3 of acetone and 5 cm^3 of an aqueous solution containing 15% by weight of $Na_2S_2O_4$ in aqueous NaOH (10% by weight) were added to 200 cm^3 of the diesel oil marked as above; after stirring for 20 seconds, the solution was decanted for 10 minutes, thereby obtaining a deep red aqueous layer on the bottom.

EXAMPLE 2 (Blank, comparative example)

Example 1 was repeated, by carrying out the test on the same diesel oil, without any admixture of the marking solution, the final bottom layer was light brown.

EXAMPLE 3

100 cm^3 of diesel oil, marked as in example 1, were admixed with 900 cm^3 of previously unmarked diesel oil, thus reducing the amount of marker to 3 mg/dm^3; the colorimetric test caused formation of a final bottom layer still red, the intensity of which was much lower than that obtained in example 1.

EXAMPLE 4

100 cm^3 of unmarked diesel oil, 20 cm^3 of acetone and 10 cm^3 of the dithionite solution of example 1 were added to 100 cm^3 of diesel oil marked as in example 1; after stirring and decanting, the bottom phase was collected in a volumetric flask. The absorption intensity, after filtration, was determined at 50 nm (nanometer). A calibration plot allowed to confirm with precision the original marker concentration.

EXAMPLE 5

1 g of a composition, obtained by mixing 8 g of 2-ethyl-anthraquinone, 8 g of furfural, 64.8 g of an anthraquinone dye (known according to the COLOR INDEX as "solvent green 33"), and 7.2 g of mixed xylenes, were added to 4 kg of a diesel oil to be used for motorboats, thus obtaining a fuel containing 20 ppm of 2-ethyl-anthraquinone. The colorimetric test of example 1 was carried out on 200 cm^3 of the thus marked oil and an aqueous bottom layer presenting a deep red color was obtained.

EXAMPLE 6

1 g of 2-ethyl-anthraquinone was added to 100 cm^3 of a mixture of xylenes and to 3 cm^3 of the thus obtained xylenic solution a gasoline to be used for motorboats in the fishing industry was added until the obtention of a 1 liter volume. The resulting solution contained 30 mg/dm^3 of 2-ethyl-anthraquinone. Thereafter, 100 cm^3 of virgin (unmarked) diesel oil, 10 cm^3 of acetone and 5 cm^3 of the dithionite solution of example 1 were added to 100 cm^3 of gasoline marked as above; the test was operated as in example 1 and a deep red aqueous layer was obtained on the bottom.

EXAMPLE 7

Example 6 was repeated while replacing gasoline by lamp oil to be used for the lighting of fishing boats. In this case the final bottom aqueous layer obtained also presented a deep red color.

EXAMPLES 8-14

Example 1 was repeated while modifying the chemical nature of the marker and its concentration; data and results are on table 1.

TABLE 1

Example	8	9	10	11	12	13	14
Substituting group:							
- R_1	hydrogen	hydrogen	methyl	hydrogen	chlorine	methyl	CH_3
- R_2	t.butyl	methyl	hydrogen	hexyl	hydrogen	hydrogen	CH_3
- R_3	hydrogen	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
- R_4	hydrogen	hydrogen	isopropyl	hydrogen	hydrogen	hydrogen	CH_3
- R_5	hydrogen	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
- R_6	hydrogen	methyl	hydrogen	hydrogen	hydrogen	hydrogen	CH_3
- R_7	hydrogen	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
- R_8	hydrogen	hydrogen	hydrogen	hydrogen	chlorine	hydrogen	CH_3
Concentration (ppm)	20	30	30	40	30	40	30
Result	positive test	positive test	positive test	positive test	positive test	positive test	positive test

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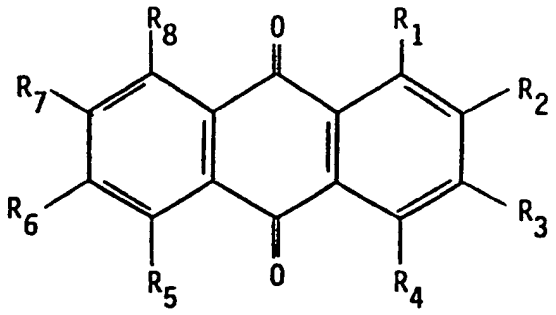
CLAIMS

1.- A marking and denaturing composition, particularly suitable for marking and denaturing oil and similar oil products, containing an anthraquinone derivative having the formula:



where R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 identical or different, represent a hydrogen atom, a halogen atom or an alkyl, cycloalkyl or arylalkyl radical having from 1 to 12 carbon atoms.

2.- Composition according to claim 1, also containing a usual dye for oil products, in particular an azoic dye and/or an anthraquinone dye.

3.- Composition according to claim 1, also containing as a diluent furfural and/or suitable organic solvents, for example xylenes.

4.- A marking and denaturing composition suitable for marking diesel oil, containing 2-ethyl-anthraquinone and preferably further containing a suitable organic solvent as a diluent.

5.- Composition according to claim 4, further containing furfural and/or an anthraquinone dye.

6.- Marked diesel oil containing from 1 to 300 ppm and preferably from 3 to 50 ppm of 2-ethyl-anthraquinone, preferably in admixture with furfural and/or with an anthraquinone dye.

7.- A method for marking and/or denaturing diesel oil or other similar oil product, wherein the anthraquinone derivative of claim 1 is added to the product to be marked and/or denatured, preferably in admixture with furfural, with an anthraquinone dye and with a proper solvent, for example xylenes.

8.- A method according to claim 7, wherein the amount of said anthraquinone derivative is comprised between 1 and 300 ppm, and preferably between 3 and 50 ppm, with respect to the oil product to be marked and/or denatured.

European Patent Office

EUROPEAN SEARCH REPORT

0201368
Application number

EP 86 40 0642

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A- 851 639 (ESSO) * Claims 1-4,6; page 1, lines 32-47 *	1,2,7	C 10 L 1/00 C 10 L 1/18 C 10 L 1/20
Y		3	
A	BE-A- 524 604 (SEIFERT VAN DER MERWEDE) * Claims 1,2,9,10; page 1, lines 5-7 *	1,7	
Y	GB-A- 361 310 (HOWARD FERGUSON) * Claim 1; page 1, lines 35-39 *	3	
A	US-A-3 164 449 (BUXBAUM) * Claims 1,9,10; column 1, line 35 - column 2, line 9; column 2, line 64 - column 3, line 3; column 3, line 68 - column 4, line 6 *	1-3,7	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 L C 09 B
A	DE-C-2 702 985 (BASF) * Claims 1,3; column 4, lines 35-45 *	1-7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-06-1986	DE LA MORINERIE B.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(12) # EUROPEAN PATENT SPECIFICATION

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(54) **Marking and denaturing composition, particularly suitable for marking and denaturing diesel oil and similar oil products.**

(30) Priority: **12.04.85 IT 2031685**

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(56) References cited:
BE-A- 524 604
DE-C- 2 702 985
GB-A- 361 310
GB-A- 851 639
US-A- 3 164 449

(73) Proprietor: **BASF Italia SpA**
Via Vincenzo da Seregno, 44
I-20161 Milano MI (IT)

(72) Inventor: **Prandi, Carlo**
6 Via Donegani
I-20020 Cogliate Milan (IT)
Inventor: **Osti, Alberto**
53 Via Rombon
I-20134 Milan (IT)

(74) Representative: **Schweiss, Werner, Dr. et al**
BASF Aktiengesellschaft Patentabteilung ZSP - C 6
D-6700 Ludwigshafen (DE)

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Description

The invention relates to marked diesel oil and a method for marking diesel oil and similar oil products.

There is currently a need for marking oil products (for example fuels or industrial solvents) due to the difference in price at which that same product may be offered for sale. Indeed, as a consequence of different rates of taxation, diesel oils intended e. g. for agricultural purposes, or diesel oils intended for the fishing industry are taxed at a lower rate than diesel oil intended for road vehicles and such a situation is liable to give rise to fiscal fraud, when the product is furnished for purposes different to those provided for by the fiscal regulations. This is in fact why the products are usually marked by means of suitable compounds, which allow an easy identification. An ideal marker should exhibit the following features :

- a satisfactory stability under conditions of normal use ;
- no impairing of the physico-chemical features of the petroleum fuel or of the solvent ;
- a solubility sufficient to allow use in the form of a concentrated solution ;
- very low chances of being eliminated by means of physical or chemical methods ;
- possibility of being used in small quantities ;
- possibility of being identified by means of simple, quick and very sensitive methods ;
- absence of negative toxicological features.

Not all proposed or used marking compositions can completely satisfy such requirements. In fact, the best known markers are :

- radioactive substances, requiring particular care, during handling, because of physiological dangers ;
- metallorganic compounds, generally showing a poor stability during storage ;
- furfural, which could also be present as traces naturally occurring in the oil cuts, and thus give rise to a positive test due simply to the particular kind of analysis (furfural, moreover, shows poor stability) ;
- diphenylamine, which can be rather easily eliminated ; since it is an amino-aryl compound, diphenylamine must be handled in a carefully strictly controlled zone ;
- primary, secondary or tertiary arylamines, which can easily be extracted by means of diluted acids ; as with the case of diphenylamine, their handling is controlled by very strict regulations ;
- naphthols, which could already be present within the oil cuts and which can easily be eliminated.

U. S. Patent 4 209 302 discloses the use of naphthylamine derivatives. However, these compounds do not completely satisfy the requirements herein-above, especially because they can easily be extracted from the marked product.

It is an object of the present invention to provide marked diesel oil or other similar products which do not exhibit the disadvantages of such products marked in a conventional manner, and a method for marking diesel oil and similar oil products.

Accordingly, the present invention relates to marked diesel oil or similar oil products containing from 1 to 300 ppm of 2-ethylanthraquinone, 2-tert-butylanthraquinone, 1-methyl-4-isopropylanthraquinone, 2-hexylanthraquinone, 1,8-dichloroanthraquinone, 1, 3, 5, 7-tetramethylanthraquinone or hexamethylanthraquinone.

The diesel oil and/or similar oil products marked according to the present invention have the following advantages :

- no counter-indications of toxicological nature ;
- considerable stability of the marker with respect to the oil product to be marked ;
- difficulty to eliminate the said marker from its solutions within the oil products, by means, for example, of adsorption techniques on active carbons, alumina, decoloring earth or silica gel ;
- no modification of color of the oil product, whereby the presence within diesel oil can be ascertained only when carrying out a specific test ;
- the marker can be identified and determined quantitatively by means of very simple methods that do not require complicated devices and can be carried out by unskilled personnel ; and
- the marker can be handled either as a solid or as a solution in organic solvents, optionally in admixture with other colored or colorless markers.

The marking method according to the present invention should be prescribed, in particular, when an anthraquinone dye and/or an azoic dye is present in the diesel oil, etc. ; best results are obtained when the diesel oil or other similar oil product contains furfural and/or other suitable organic solvents, for example xylenes, these xylenes generally acting as a diluent.

Oil products similar to diesel oil are, for example, gasoline, kerosene oil and lamp oil.

The amounts of anthraquinone derivative to be used as a marker can vary within wide limits and the

minimum value merely depends upon the indentification test. By using the simple and rapid test described hereinafter, concentrations as low as 1 to 3 ppm can be used.

Generally, a greater amount is added, in order to obtain in any case a positive result and also to foresee the case where the marked product is diluted at the time the fraud occurs. From a practical point of view, from 1 to 300 ppm and preferably 3-50 ppm can be used.

As to the method of identifying the products it is preferable to operate according to the following method :

— 10 cm^3 of acetone and 5 cm^5 of an aqueous and alkaline solution of sodium dithionite are added to 200 cm^3 of marked diesel oil which is thereafter stirred and left to decant for 5-10 minutes, whereby the bottom layer presents a red color characteristic of the claimed anthraquinone derivative.

The following Examples illustrate the invention.

Example 1

1 g of 2-ethyl-anthraquinone was added to 100 cm^3 of a mixture of xylenes and to 3 cm^3 of the solution thus obtained a diesel oil, intended for motorboats, was added until 1 liter volume was obtained, i. e. a solution containing 30 mg/dm^3 (30 ppm) of 2-ethyl-anthraquinone. Thereafter, 10 cm^3 of acetone and 5 cm^3 of an aqueous solution containing 15 % by weight of $Na_2S_2O_4$ in aqueous NaOH (10 % by weight) were added to 200 cm^3 of the diesel oil marked as above ; after strirring for 20 seconds, the solution was decanted for 10 minutes, thereby obtaining a deep red aqueous layer on the bottom.

Example 2 (Blank, comparative example)

Example 1 was repeated, by carrying out the test on the same diesel oil, without any admixture of the marking solution, the final bottom layer was light brown.

Example 3

100 cm^3 of diesel oil, marked as in Example 1, were admixed with 900 cm^3 of previously unmarked diesel oil, thus reducing the amount of marker to 3 mg/dm^3 ; the colorimetric test caused formation of a final bottom layer still red, the intensity of which was much lower than that obtained in Example 1.

Example 4

100 cm^3 of unmarked diesel oil, 20 cm^3 of acetone and 10 cm^3 of the dithionite solution of Example 1 were added to 100 cm^3 of diesel oil marked as in Example 1 ; after stirring and decanting, the bottom phase was collected in a volumetric flask. The absorption intensity, after filtration, was determined at 500 nm (nanometer). A calibration plot allowed to confirm with precision the original marker concentration.

Example 5

1 g of a composition, obtained by mixing 8 g of 2-ethyl-anthraquinone, 8 g of furfural, 64,8 g of an anthraquinone dye (known according to the COLOR INDEX as « solvent green 33 ») and 7.2 g of mixed xylenes, was added to 4 kg of a diesel oil to be used for motorboats, thus obtaining a fuel containing 20 ppm of 2-ethyl-anthraquinone. The colorimetric test of Example 1 was carried out on 200 cm^3 of the thus marked oil and an aqueous bottom layer presenting a deep red color was obtained.

Example 6

1 g of 2-ethyl-anthraquinone was added to 100 cm^3 of a mixture of xylenes and to 3 cm^3 of the thus obtained xylenic solution a gasoline to be used for motorboats in the fishing industry was added until the obtention of a 1 liter volume. The resulting solution contained 30 mg/dm^3 of 2-ethyl-anthraquinone. Thereafter, 100 cm^3 of virgin (unmarked) diesel oil, 10 cm^3 of acetone and 5 cm^3 of the dithionite solution of Example 1' were added to 100 cm^3 of gasoline marked as above ; the test was operated as in Example 1 and a deep red aqueous layer was obtained on the bottom.

Example 7

Example 6 was repeated while replacing gasoline by lamp oil to be used for the lighting of fishing boats. In this case the final bottom aqueous layer obtained also presented a deep red color.

Examples 8-13

Example 1 was repeated while modifying the chemical nature of the marker and its concentration; data and results are in Table 1.

Table 1

Example	8	9	10	11	12	13
Substituting group:						
R^1	hydrogen	methyl	hydrogen	chlorine	methyl	CH_3
R^2	t-butyl	hydrogen	hexyl	hydrogen	hydrogen	CH_3
R^3	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
R^4	hydrogen	isopropyl	hydrogen	hydrogen	hydrogen	CH_3
R^5	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
R^6	hydrogen	hydrogen	hydrogen	hydrogen	hydrogen	CH_3
R^7	hydrogen	hydrogen	hydrogen	hydrogen	methyl	CH_3
R^8	hydrogen	hydrogen	hydrogen	chlorine	hydrogen	CH_3
Concentration (ppm)	20	30	40	30	40	30
Result	positive test	positive test	positive test	positive test	positive test	positive test

Claims

1. Marked diesel oil or similar oil products containing from 1 to 300 ppm of 2-ethylanthraquinone, 2-tert-butylanthraquinone, 1-methyl-4-isopropylanthraquinone, 2-hexylanthraquinone, 1,8-dichloroanthraquinone, 1, 3, 5, 7-tetramethylanthraquinone or hexamethylanthraquinone.

2. Marked diesel oil according to claim 1, containing from 3 to 50 ppm of the said anthraquinone compounds.

3. Marked diesel oil according to claim 1 or 2, additionally containing furfural and/or an anthraquinone dye.

4. Marked diesel oil according to claim 1, 2 or 3, containing 2-ethylanthraquinone.

5. A method for marking and/or denaturing diesel oil or other similar oil products, wherein 2-ethylanthraquinone, 2-tert-butyl-anthraquinone, 1-methyl-4-isopropylanthraquinone, 2-hexylanthraquinone, 1,8-dichloroanthraquinone, 1, 3, 5, 7-tetramethylanthraquinone or hexamethylanthraquinone is added to the product to be marked and/or denatured with a proper solvent.

6. A method according to claim 5, wherein furfural and/or anthraquinone dye are additionally added.